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THE PHOTOLYSIS OF CO_2 AT 1849 AND 2139A

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D. Krezenski, R. Simonaitis and J. Heicklen

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ABSTRACT

The quantum yield for the photodissociation of CO_2 at $25^{\circ}C$ is 1.08 ± 0.12 for direct photolysis at 1849 A and CO_2 pressures between 200 and 800 torr; 0.48 ± 0.02 for the Hg $6(^1P_1)$ sensitized decomposition at CO pressures between 130 and 730 torr; and 0.16 ± 0.05 for the direct photolysis at 2139 A and CO_2 pressures between 300 and 600 torr. At these wavelengths there is insufficient energy to produce $O(^1D)$, and the primary process is

$$CO_2 + h\nu \rightarrow CO + O(^3P)$$

INTRODUCTION

The principal atmospheric component of both Mars and Venus is CO_2. Therefore the photochemistry of this molecule is important in the atmospheres of these planets. Previous investigations[1,2] have shown that the primary photochemical process at 1470 and 1236A is

$$CO_2 + h\nu \rightarrow CO + O(^1D) \qquad 1$$

and that this process proceeds with unit quantum efficienty. We have now examined the photodissociation of CO_2 at wavelengths with insufficient energy (λ>1658A) to produce $O(^1D)$ atoms and have found that at 25°C photodissociation occurs. Presumably the primary process is

$$CO_2 + h\nu \rightarrow CO + O(^3P) \qquad 2$$

The quantum yield is 1.08 ± 0.12 for the direct photolysis at 1849A and CO_2 pressures between 200 and 800 torr; 0.48 ± 0.02 for the Hg $6(^1P_1)$ sensitized decomposition at CO pressures between 130 and 730 torr; and 0.16 ± 0.05 for the direct photolysis at 2139A and CO_2 pressures between 300 and 600 torr.

Two studies of the direct photodissociation in this region have been reported recently. DeMore[3] found that for CO_2 pressures of 400 psi, the quantum yield of CO production, $\Phi\{CO\}$, was unity, but Inn[4] reported $\Phi\{CO\}$ = 0.70 at 29-142 torr of CO_2 for radiation between 1750 and 1850A. Our results, done at intermediate pressures, support the former measurement. Mori[5] found that CO was produced in the Hg $6(^1P_1)$ sensitized photolysis of CO_2 at 1849A, but quantum yields were not reported.

EXPERIMENTAL

The gases used were Matheson NO, N_2O, and Bone-Dry CO_2. The CO_2 and NO were purified by distillation at -130°C and -186°C, respectively. All three were degassed at -196°C immediately before use.

The reactions were carried out at 25°C in a cylindrical quartz cell 5 cm in diameter and 10 cm long which was connected to a grease free high vacuum line. For the direct irradiations the vacuum line was also Hg free, as ascertained from the lack of product formation from N_2O photolysis at 2537A. Radiation was from either a Hanovia flat-spiral mercury resonance lamp model No. Z1400-013 (1849A) or a Phillips Zn resonance lamp model No. 93106E (2139A).

For the Hg-sensitized experiments, a drop of mercury was placed in the reaction cell. The Hanovia lamp was enclosed in a cylindrical container and continuously flushed with N_2 to purge O_2, which absorbs radiation at 1849A. The radiation was also filtered by a LiF window which had been irradiated with a Co-60 source. In this way 2537A radiation was considerably reduced,[6] so that N_2O actinometry could be employed.

After photolysis, the gases noncondensable (CO, O_2, N_2) at -196°C were collected and analyzed by gas chromatography utilizing a 1/4-inch diameter column with 5A molecular sieves and a Gow Mac 40-05D power supply in conjunction with thermistor detectors. In the Hg-free system an aliquot was taken, whereas in the Hg-sensitized experiments the whole sample was collected in a Toepler pump.

Actinometry was done with N_2O which photodissociates to give a quantum yield of N_2 formation of 1.41 for all the conditions of this study.[7] For the direct irradiations, the absorbed intensity, I_a, was obtained by using pressures of N_2O to exactly match the absorbance at corresponding CO_2 pressures. In this way all geometrical corrections are eliminated. The extinction coefficients used are listed in Table I. Since both absorption spectra are virtually continuous above 1800A, the fact that we used line sources should not introduce errors. For the mercury-sensitized experiments, the absorption of radiation is complete. Actinometer experiments were done with pressures of N_2O equal to those of CO_2 to insure that any pressure-broadening effects would cancel.

RESULTS

The products of the direct photolysis of CO_2 at 1849A were CO and O_2. The results are shown in Table II. Experiments were done with CO_2 pressures between 200 and 800 torr for irradiation times of 5 to 784 minutes. The measured values for $\Phi\{CO\}$ were slightly greater than unity and were invariant to changes in the reaction parameters. The reaction sequence is presumably

$$CO_2 + h\nu \rightarrow CO + O(^3P) \qquad 2$$

$$O(^3P) \rightarrow (1/2)\ O_2 \qquad 3$$

The mechanism predicts that $\Phi\{CO\} = 1.0$ which is nearly obeyed, and that $[CO]/[O_2] = 2.0$. The measured values of the ratio $[CO]/[O_2]$ are significantly greater than 2.0, thus showing that some of the $O(^3P)$ atoms are lost at the walls. Such an effect was observed at lower wavelengths in other studies,[2] as well as in our laboratory in a different system.[10] In an attempt to minimize the wall loss, small amounts of NO were added in a few experiments to aid O_2 production via

$$O + NO + M \rightarrow NO_2 + M \qquad 4$$

$$O + NO_2 \rightarrow NO + O_2 \qquad 5$$

These experiments yielded slightly, but not significantly, better results. The average of all the experiments gives $\Phi\{CO\} = 1.08 \pm 0.12$ and $[CO]/[O_2] = 2.25 \pm 0.19$.

In the mercury-sensitized decomposition of CO_2, again CO and O_2 were produced. However $\Phi\{CO\}$ dropped markedly as the irradiation time was lengthened, the O_2 deficiency was large ($[CO]/[O_2] = 2.6$-12), and HgO was produced. These results agree with those found by Mori,[5] and can be explained by the fact that $O(^3P)$ ultimately becomes HgO rather than O_2. As the HgO accumulates on the cell windows, the absorbed intensity (and thus the apparent quantum yield) drops. This was confirmed in separate actinometer experiments.

In order to avoid HgO formation, photolyses were done with 0.8-1.0 torr of NO added to produce O_2 via reactions 4 and 5. The resultant quantum yield of CO formation, $\Phi\{CO\}$ was then independent of irradiation time and CO_2 pressures (130-730 torr). The results are in Table III, and the average value for $\Phi\{CO\}$ is 0.48 ± 0.02. Since $\Phi\{CO\}$ is much less than one, about one half of the Hg $6(^1P_1)$ quenching by CO_2 is by physical, rather than chemical quenching.

A few runs were done with 2139A radiation. The absorption was very small which necessitated very long runs ($\sim$40 hrs.). Thus the results are not too accurate. The average of three experiments between 300 and 600 torr of CO_2 gave $\Phi\{CO\} = 0.16 \pm 0.05$. Since this value is considerably less than one, deactivation is more important than decomposition. This result is not difficult to understand since radiation at 2139A gives only 6.4 kcal/mole in excess of that needed for dissociation of CO_2. Decomposition from the photoexcited CO_2 molecule is relatively slow, and deactivation can compete effectively.

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TABLE I

Extinction Coefficients

Gas	λ, A	ε, cm^{-1} [a]	References
CO_2	1849	7.71×10^{-3}	Ogawa[8]
CO_2	2139	0.061×10^{-3}	Ogawa[8]
N_2O	1849	3.64	Zelikoff et al.[9]
N_2O	2139	0.090	Zelikoff et al.[9]

a) Extinction coefficient for a standard atmosphere of gas at 25°C.

TABLE II

Direct Photolysis of CO_2 at 1849A and 25°C
I_a = 5.3 μ/min.

$[CO_2]$, torr	Irradiation time, min.	$\Phi\{CO\}$	$[CO]/[O_2]$
200[a]	30.0	0.99	1.88
400[b]	30.0	1.05	1.98
400[b]	60.0	0.99	2.34
760	5.0	1.38	2.06
790	15.0	1.43	2.35
725	15.0	1.05	2.20
741	30.0	0.97	2.28
700[c]	30.0	0.92	1.96
775	45.0	1.05	2.50
750	60.0	1.01	2.68
740[d]	60.0	1.02	2.15
710[c]	90.0	1.16	2.23
750	91.0	1.14	2.50
800	120.0	1.29	-
690[c]	180.0	0.99	2.43
790	784.0	0.83	-
		ave. = 1.08 ± 0.12	2.25 ± 0.19

a) I_a = 1.36 μ/min.

b) I_a = 2.9 μ/min.

c) 30μ NO also present.

d) 16μ NO also present.

TABLE III

Hg-photosensitized Decomposition of CO_2 at 1849A and 25°C in the presence of 0.8-1.0 torr of NO. $I_a = 7.35\ \mu/\text{min}$.

$[CO_2]$, torr	Irradiation time, min.	$\Phi\{CO\}$
130	15.00	0.46
213	15.00	0.47
401	15.00	0.46
410	10.00	0.51
420	2.00	0.50
730	15.00	0.51
		ave. = 0.48 ± 0.02